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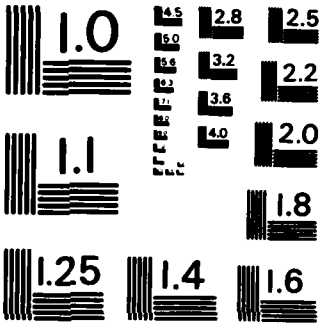

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ELECTROCHEMISTRY OF RARE-EARTH DIPHTHALOCYANINES

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Lutetium diphthalocyanine films on tin oxide electrodes in several aqueous chloride electrolytes were investigated by cyclic voltammetry and *in situ* visible-range absorption spectroscopy at controlled potentials. Although several redox processes of the dye film were evident in the voltammograms, they were more clearly resolved in the spectroelectrochemical data, from which equilibrium potentials corresponding to fifty percent conversion between successive oxidation states were determined. These potentials in hydrochloric acid electrolytes varied with the hydrogen ion or chloride ion activity in accordance with the Nernst equation written for incorporation of ions in the film to compensate the gain or loss of electrons. (continued)

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19. ABSTRACT (Continued)

The absorption spectra of the various colored products in hydrochloric acid matched those observed previously for discrete oxidation states of lutetium diphthalocyanine. Reduction in tetrabutylammonium chloride showed evidence of slower electrode kinetics and led to products with more complex absorption spectra. The dark blue and violet reduction products containing hydrogen ion were rapidly oxidized in air but stable with air absent. A lighter blue form which initially contained potassium ion appeared to undergo cation exchange with tetrabutylammonium ion on open circuit, resulting in a product of moderate oxygen sensitivity.

CONTENTS

TABLES

FIGURES

I. INTRODUCTION

A program to investigate the electrochromic behavior of rare-earth diphthalocyanines was begun in this laboratory in 1977 under sponsorship of the Air Force Office of Scientific Research. These dye compounds, in the form of thin films on transparent electrodes, undergo a series of at least four rapid, reversible color changes as a result of discrete electron-transfer reactions. For lutetium diphthalocyanine, the principal color states include the initial green form, an orange or reddish oxidation product, and light blue, dark blue, and violet reduction products. Such multicolor electrochromism within a solid material is unusual and is expected to find applications in a variety of flat-panel information displays and other electro-optical devices.[1-5]

This report covers a one-year contract period ending in April 1984. Among the highlights of the research in prior years[6,7] are: A radiotracer study of the ion-insertion processes that compensate for electron transfer[8]; a galvanostatic transient investigation of the electrode kinetics revealing space-charge control of the orange/green process at high current densities[9]; a kinetic study of slow spontaneous color reversal in oxidized films exposed to air[10]; cyclic voltammetric measurements indicating a major phase change associated with the light blue/dark blue transformation in a hydrochloric acid electrolyte[7]; and spectroscopic evidence of reversible oxygen addition to lutetium diphthalocyanine in dimethylformamide solution.[7] Although some points remain to be clarified, a consistent scheme for the stoichiometries and mechanisms of the lutetium diphthalocyanine redox system has emerged from these results, in combination with those of related Rockwell Navy programs[11-13] and research efforts in other laboratories.[1,14-16] Electrochemistry of the diphthalocyanines through mid-1981 is reviewed in Reference 1. In the present reporting period, equilibrium potentials were determined for the various couples in the lutetium system, and further information was obtained on the voltammetric behavior and sensitivity to oxygen.

II. STATEMENT OF WORK*

a. Investigate vacuum deposited diphthalocyanine films in contact with aqueous electrolytes of selected ion types and pH values.

b. Electrochemically convert the films to oxidized and reduced forms, and measure electrochemical characteristics of the film conversion processes at equilibrum and under current flow.

c. Supplement electrochemical measurements by *in situ* optical absorption spectroscopy.

d. Interpret data to obtain electrochemical thermodynamic and preliminary kinetic information on diphthalocyanine electrochromic systems.

e. Determine effects of oxygen on film absorption spectra at selected pH values.

*Contract F49620-83-C-0088

III. RESULTS

Part A of this section indicates the content of a forthcoming paper on the role of oxygen in the redox chemistry of the rare-earth diphthalocyanines. Part B summarizes the results of a recent spectroelectrochemical investigation of equilibrium potentials for lutetium diphthalocyanine films in contact with selected aqueous chloride electrolytes and gives related cyclic voltammetric data. Finally, the behavior of reduced forms of the dye on open circuit before and after exposure to oxygen is briefly discussed.

A. THE ROLE OF OXYGEN

Spectroscopic evidence on the role of oxygen in the redox chemistry of lutetium diphthalocyanine is reported in a paper that has been accepted for publication in the Journal of the Electrochemical Society. The observations indicate an irreversible reaction of oxygen with vacuum-sublimed films of the green dye material and a reversible reaction with its solution in dimethylformamide. This behavior can account for several apparent anomalies found in previous investigations. A longer summary is given in a previous report.[7] Part B-3 of this section presents more recent information concerning effects of oxygen on electrochemically reduced lutetium diphthalocyanine films.

B. SPECTROELECTROCHEMICAL INVESTIGATION OF LUTETIUM DIPHTHALOCYANINE

Some approximate equilibrium potentials for the redox processes of lutetium diphthalocyanine films were determined in an earlier project supported by the Office of Naval Research, which had as its primary objective the quantitative characterization of colors for electrochromic display purposes.[2] In that work, it was found that the pH-potential-color relationships for the dye film in a number of buffered acidic electrolytes containing 1M KCl could be presented as a

Pourbaix-type[17] diagram with pH-potential lines drawn at the conditions corresponding to 50% conversion between adjacent color states. Although some of those lines were clearly defined, there were regions, in the vicinity of pH 4 and at strongly cathodic potentials for pH < 4, where further information was needed to complete the plot or to provide a more extensive scheme for the relationships involved. The present investigation yielded more precise equilibrium potentials for electrolytes of simpler compositions and led to improved resolution of the cathodic processes.

The cell and electrodes were similar to those described in Reference 2. The dye films, with initial absorbances in the range of 1.1 to 1.2, were prepared by vacuum sublimation on transparent pyrolytic tin oxide. The area of dye exposed to the electrolyte was approximately 2 cm^2. The reference and counter electrodes were silver-silver chloride, placed directly in the cell solution. All potentials are reported, however, with respect to the silver-silver chloride electrode at a chloride ion activity of 1M. The cell cover was redesigned for easy removal, and deaeration was accomplished by passage of nitrogen through the solution. The electrolytes used were hydrochloric acid at 0.001 to 0.1M, 0.1M tetrabutylammonium chloride (TBACl), and several KCl-TBACl mixtures. To simplify the ionic content of the system, no buffering components were used. For each electron-transfer process, the visible absorption spectrum was recorded in situ at a series of controlled potentials after equilibrium had been established with respect to the dye reaction. The main objective was to find, for each faradaic couple, the equilibrium potential $E_{0.5}$ at which the same number of dye molecules existed in the oxidized and reduced forms.

Detailed results of the equilibrium-potential study will be given in a manuscript for publication. Therefore, only a summary is provided below, in context with related information obtained by slow-scan cyclic voltammetry.

1. HCl Electrolytes

The electrochromic film in dilute HCl solutions produced well-formed absorption spectra with distinct sets of isosbestic points* for each faradaic process. A significant example of the spectral curves is given in Figure 1, where the light blue/dark blue and dark blue/violet couples were resolved spectrally, even though their $E_{0.5}$ values were separated by only 0.03 V. This distinction would be difficult to make by electrochemical methods alone.

The cyclic voltammograms in HCl, represented by Figure 2, were rather complex and included a large capacitive component in the background. Although such traces were useful in locating the faradaic transitional regions, they did not afford good estimates of $E_{0.5}$ in the cathodic potential range. Values of $E_{0.5}$ were obtained, to ±0.01 V in most cases, by plotting the optical absorbance A_λ at a selected wavelength λ as a function of the applied potential and locating the point at which half of the absorbance change for the complete process had occurred. In most instances, these curves were S-shaped, but they could be converted to linear form by plotting E vs $\log[x/(1-x)]$ where E is the applied potential and x is the fraction of dye molecules converted after equilibration, as determined from the absorption spectrum. The slope of such a plot could be used to determine an activity function for the dye species in the film, and the potential at which $\log[x/(1-x)] = 0$ provided an alternate means for evaluation $E_{0.5}$.

Table 1 gives the values of $E_{0.5}$ determined in the various electrolytes from direct plots of E vs A_λ. These potentials, for the hydrochloric acid series, were related to the activity $a_\pm$ of the acid as predicted from the Nernst equation: For reductions of the green dye, in which hydrogen ions were incorporated as the counter ions, the slopes $dE_{0.5}/d(-\log a_\pm)$ were near -59 mV per logarithmic unit. For the oxidation of the green species to orange, utilizing chloride ions, the expected reverse slope, near +59 mV, was found. In contrast to these

*Common intersection points

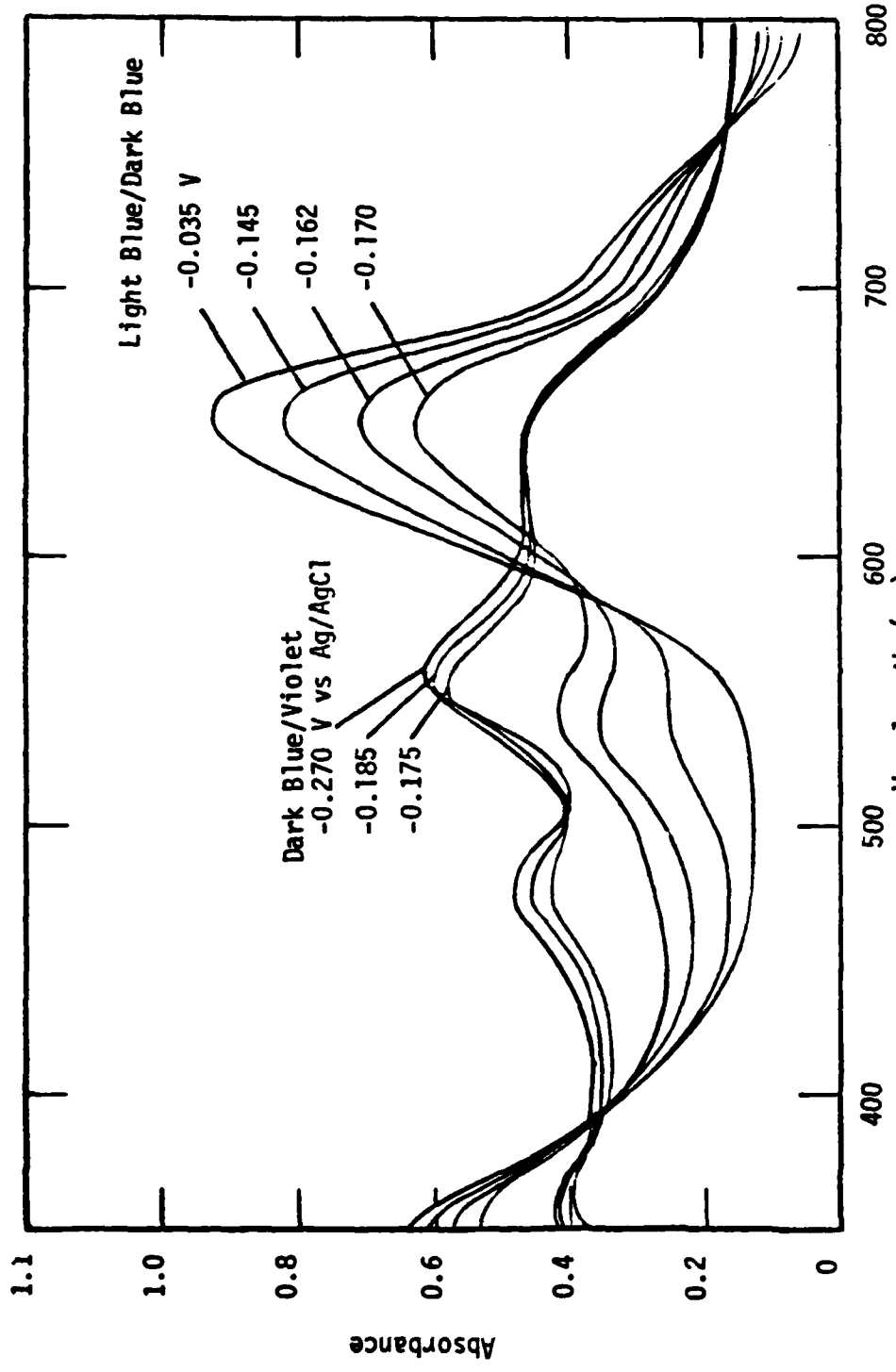

Figure 1. Absorption Spectra for Light Blue/Dark Blue and Dark Blue/Violet Couples of Lutetium Diphthalocyanine at Various Equilibration Potentials in 0.1M HCl

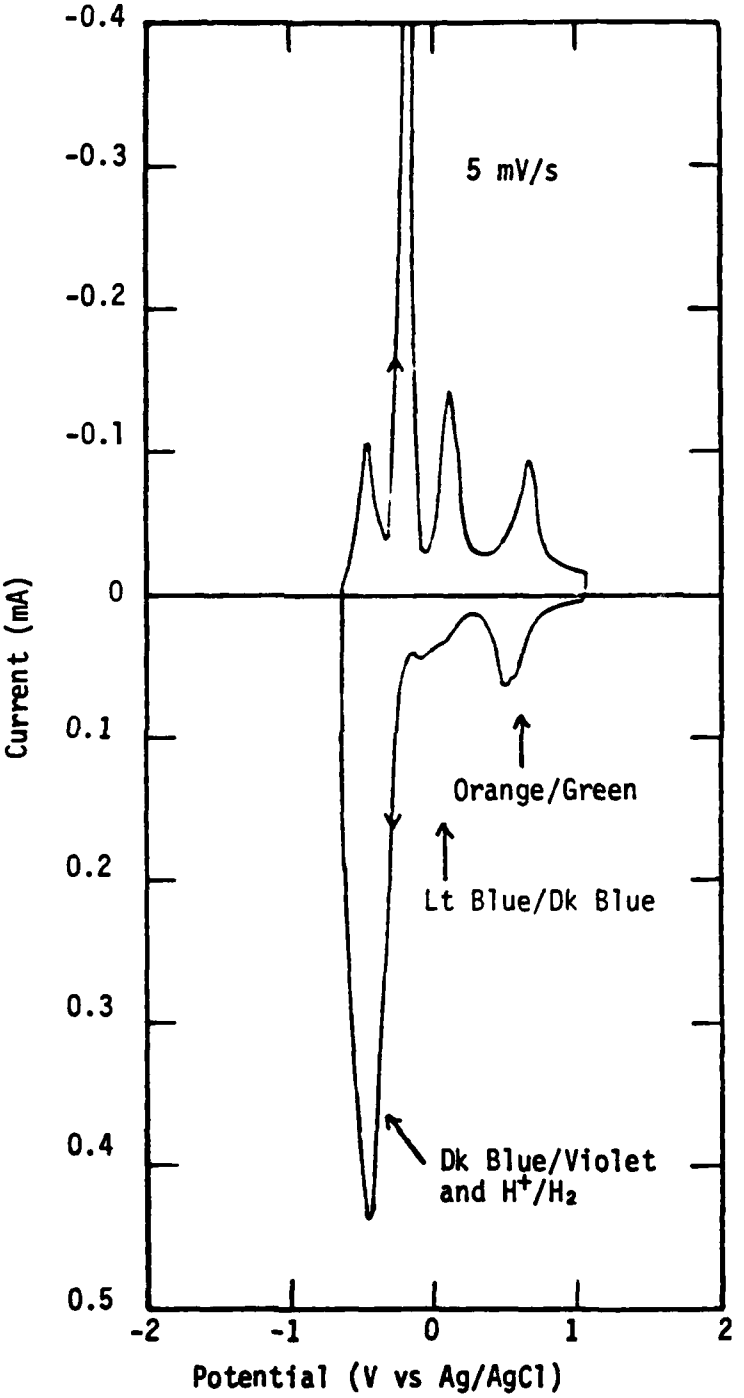

Figure 2. Wide-Span Cyclic Voltammogram for Lutetium Diphthalocyanine/Tin Oxide Electrode in 0.01M HCl

TABLE 1

EQUILIBRIUM POTENTIALS OF THE LUTETIUM DIPHTHALOCYANINE FILM SYSTEM IN AQUEOUS CHLORIDE ELECTROLYTES NEAR 25°C

Electrolyte (moles/liter)			$E_{0.5}$ (V vs Ag/AgCl,1M Cl^-)				
HCl	TBACl	KCl	O/G[a]	G/LtB	LtB/B	LtB/DkB	DkB/V
0.001	0	0	0.69	-0.04	-0.37	--	--
0.01	0	0	0.57	0.09	--	-0.23	-0.26
0.033	0	0	0.56	0.10	--	-0.22	-0.25
0.1	0	0	0.56	0.14	--	-0.15	-0.18
0	0.1	0	0.60	-0.05[b]	<0.8[b]	--	--
0	0.1	0.001	--[c]	-0.02	-0.86	--	--
0	0.1	0.01	--[c]	0.02	-0.84	--	--
0	0.01	0.1	--[c]	-0.45	--	--	--

[a]Color symbols and electrons gained relative to cycled green state are: O (orange -1); G (green, 0); LtB (light blue, +1); B (additional blue, probably +2); DkB (dark blue, +3); V (violet, probably +4).

[b]Blues with TBACl have 3 peaks evident in Q-band.

[c]$E_{0.5}$ not determined for O/G.

results, Pourbaix slopes near -180 mV were observed previously for certain lines in the green-blue-violet region of the lutetium diphthalocyanine diagram.[2] Those earlier data were obtained in 1M KCl with some acidic buffer components present, and the steeper slopes were attributed to acid adduct formation. The behavior of the corresponding dye couples in the present study, with dilute HCl only, appeared to be simpler, but the absorption spectra for the various oxidation states were consistent with those of our previous work.

2. TBACl-KCl Electrolytes

Values of $E_{0.5}$ for the TBACl-KCl series of electrolytes are included in Table 1. Some related voltammograms are shown in Figures 3 and 4. The anodic behavior of the green dye was essentially the same in these solutions as in HCl, but the background currents were lower in relation to those of the faradaic process. This comparison is made in Figure 3. The pH in these unbuffered solutions rose from about 6 to 8 in the course of the spectroelectrochemical measurements, due to slow hydrogen evolution during the times required to obtain the spectra.

The cathodic-range voltammograms with TBACl present differed from those in HCl, and this difference in behavior was reflected in the $E_{0.5}$ values as well as the spectra. The set of voltammograms in Figure 4 shows a dependence of the reduction processes on the concentration of K^+, or the K^+/TBA^+ concentration ratio. This appeared to be a transient effect. When the dye system was allowed to equilibrate at various potentials after reduction from the green state, the spectra had a 3-part Q-band, represented by Figure 5, which was not previously seen in HCl, KCl, or various buffered electrolytes. This more complex band structure apparently was due to incorporation of the larger TBA^+ counter ion in the reduction product.

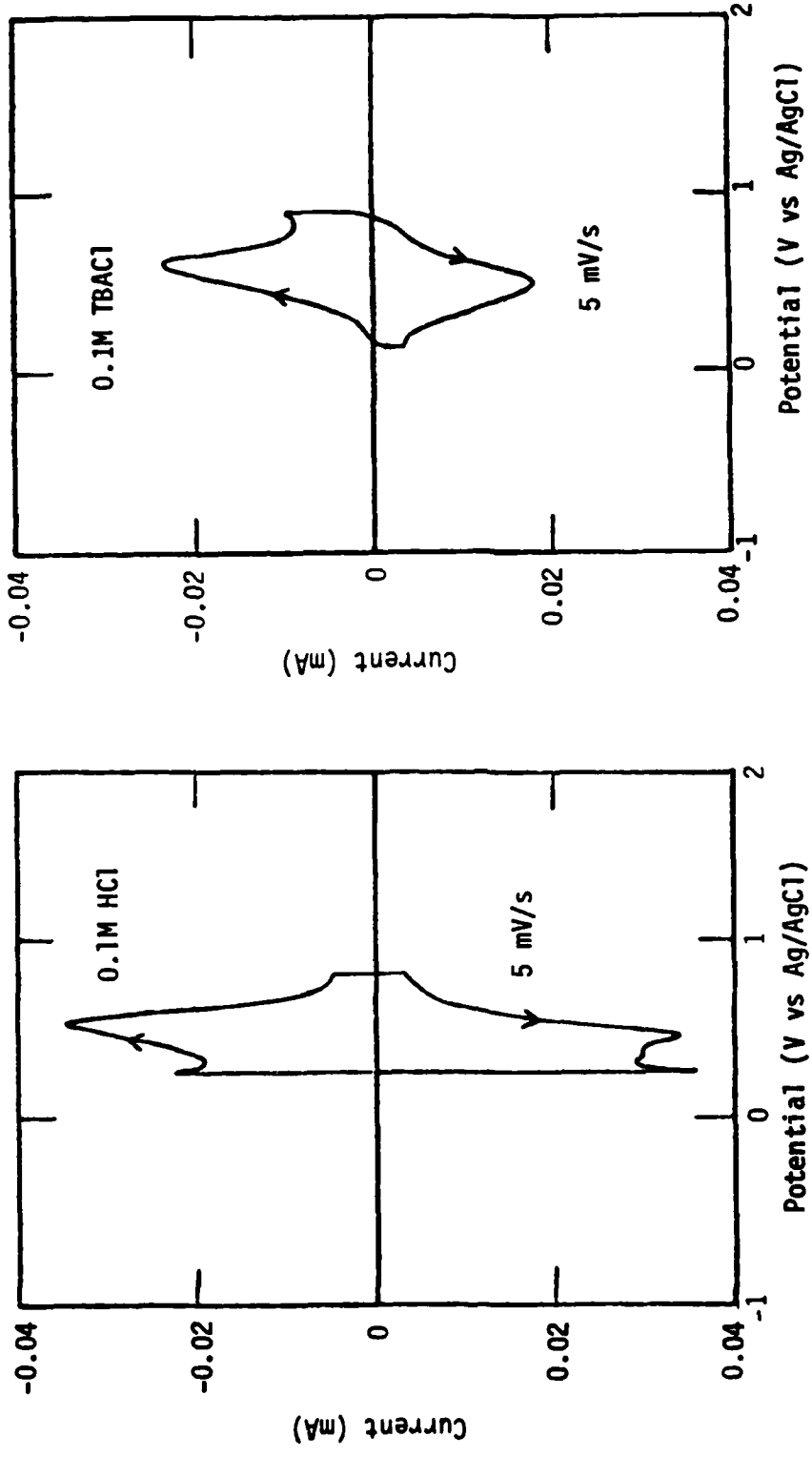

Figure 3. Cyclic Voltammograms in Anodic Potential Range for Lutetium Diphthalocyanine/Tin Oxide Electrode in 0.1M HCl and 0.1M TBACl

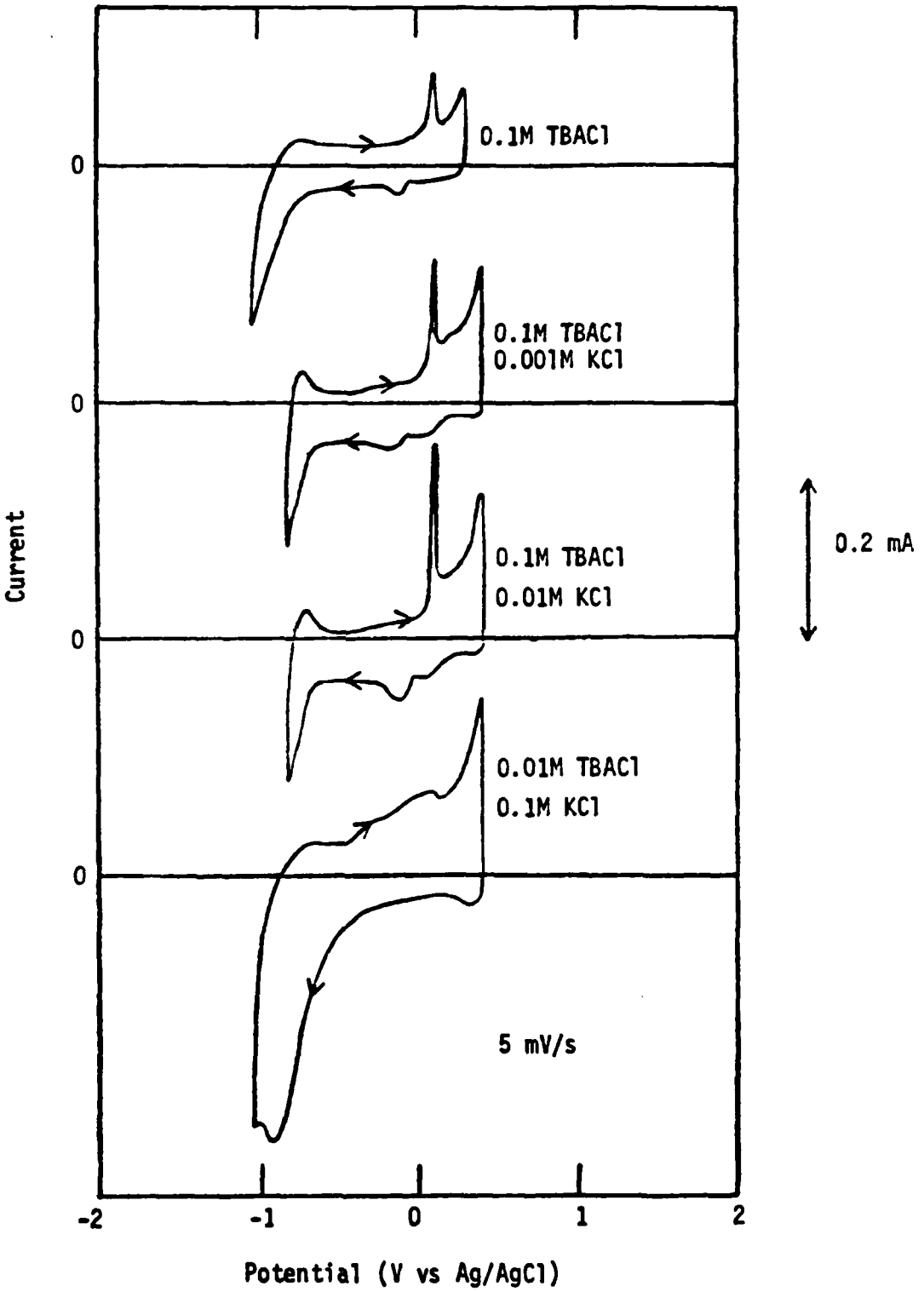

Figure 4. Cyclic Voltammograms in Cathodic Potential Range for Lutetium Diphthalocyanine/Tin Oxide Electrodes in TBACl-KCl Electrolytes

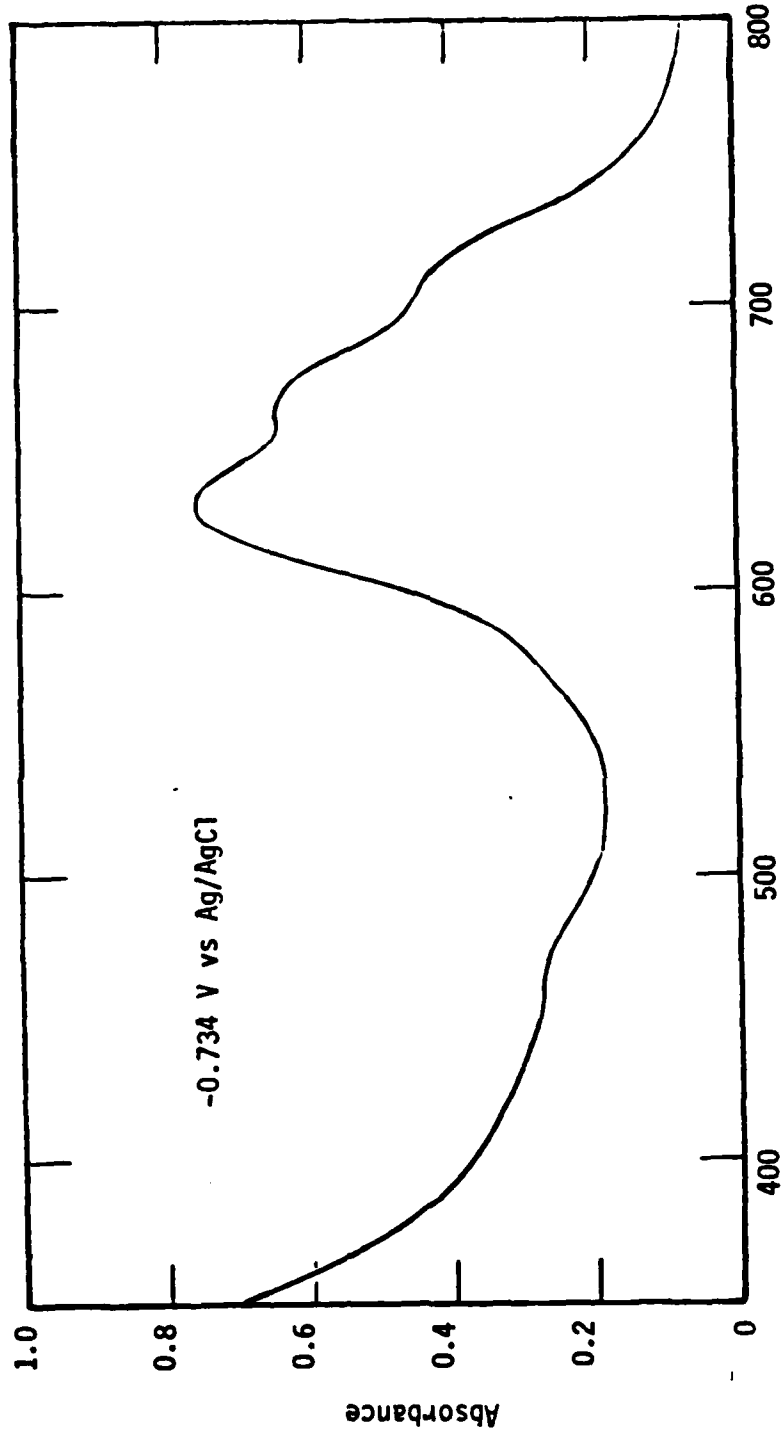

Figure 5. Absorption Spectrum of First Blue Reduction Product of Lutetium Diphthalocyanine in 0.1M TBACl + 0.001M KCl

3. Open-Circuit Behavior of Reduction Products

Possible Cation Exchange. Further observations on the electrolyte containing 0.01M TBACl + 0.1M KCl are of interest. The spectrum of the reduction product equilibrated at -0.13 V was essentially the same as that shown in Figure 5. This product resulted from a series of incremental potential changes, each followed by standing some 10 to 20 min while the spectrum was stabilized and recorded. When the same electrode was scanned directly from +0.42 V to -0.94 V at 5 mV/s, however, the reduced-film spectrum was that of Curve (a) in Figure 6. With only two peaks in the Q-band, this spectrum is typical of the product obtained by 1-electron reduction of cycled green lutetium diphthalocyanine in 1M KCl.[2] The explanation of the different spectra may be as follows: During the potential scan, which lasted 4.5 min, the bulky TBA^+ did not have time to enter the film in kinetic competition with K^+ at high concentration. Hence, the reduction near -0.02 V, using TBA^+, was bypassed, even though it was thermodynamically favored.

When this reduced electrode was placed on open circuit, its potential rose in 30 min from -1.00 V to -0.19 V. That response and the corresponding absorbance change at 635 nm are shown in Figure 7. The spontaneous change on open circuit may have been caused by the exchange of TBA^+ for K^+ in the film. Complete spectra recorded for this film at various times on open circuit are given in Figure 6.

Stability of Dark Blue and Violet Products. The dark blue and violet reduction products formed in 0.1M HCl were relatively stable on open circuit, as shown by the potential-time data in Table 2. The dark blue is a 3-electron reduction product relative to the green[2], while the violet probably is a 4-electron product. It should be recognized that some change in these materials could have resulted from slow leakage of oxygen into the cell, since it was sealed with a grease-coated rubber gasket. Visually, both products retained their colors at least 1 hr.

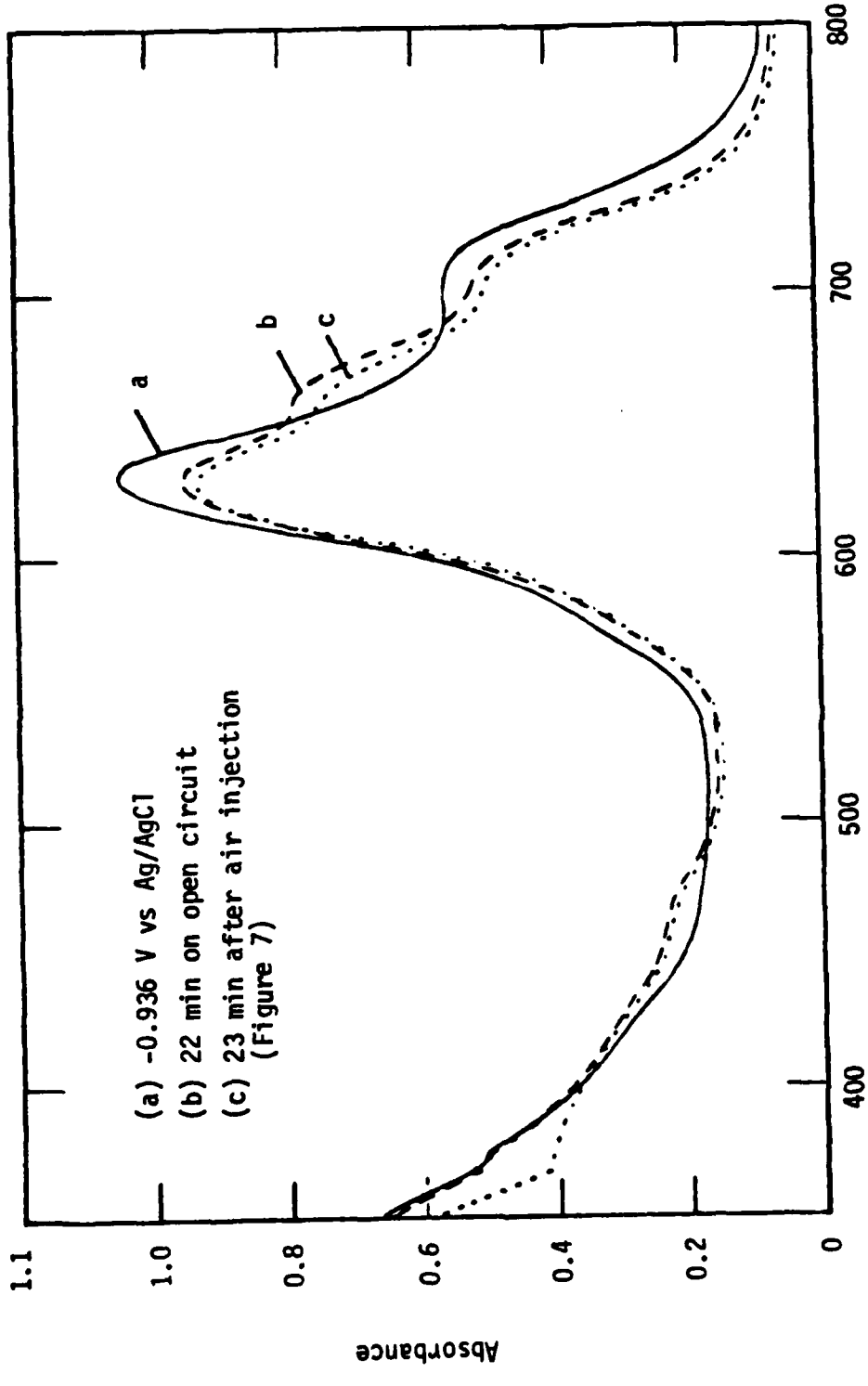

Figure 6. Absorption Spectra of First Blue Reduction Product of Lutetium Diphthalocyanine in 0.1M KCl + 0.01M TBACl

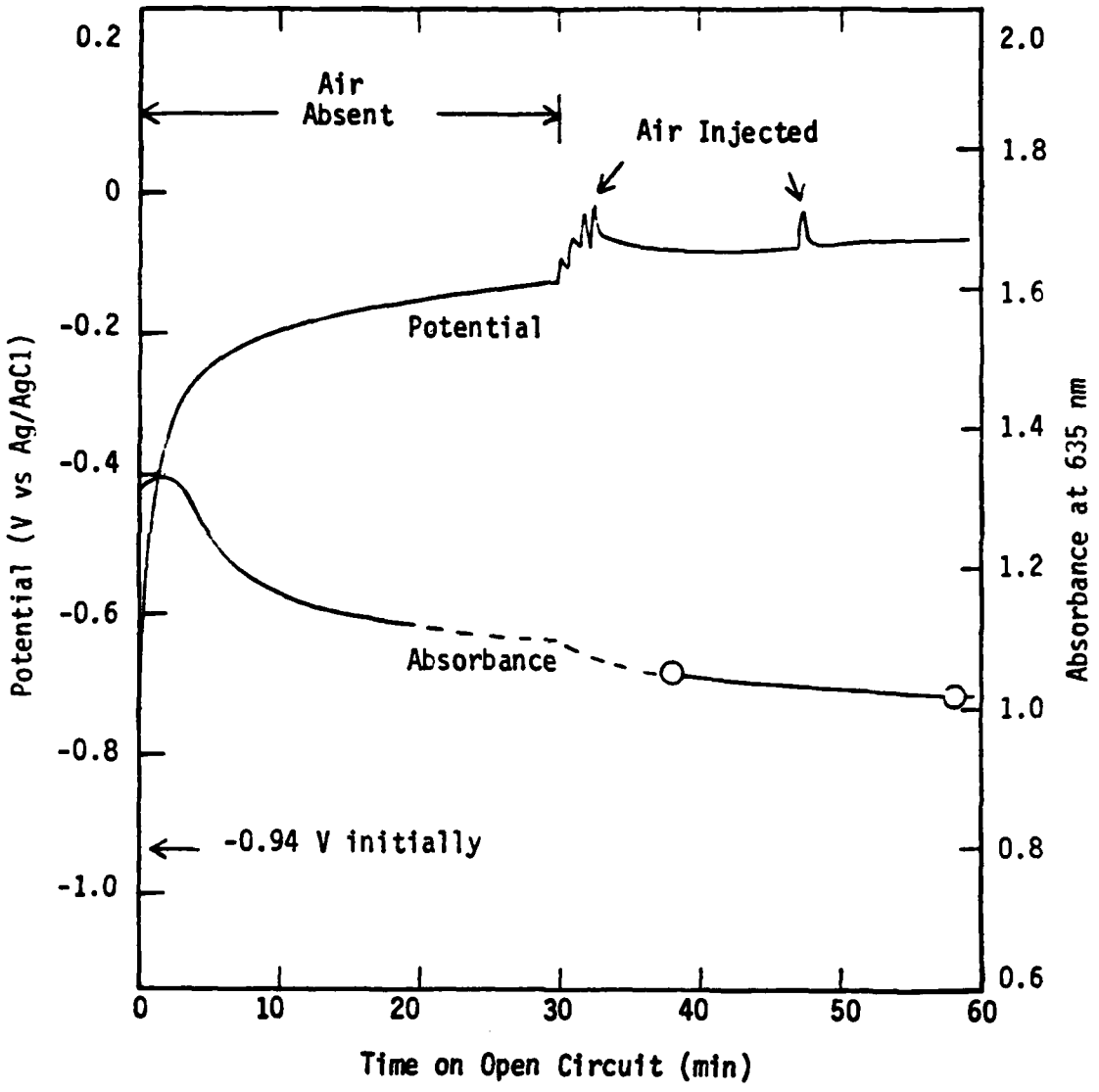

Figure 7. Open-Circuit Behavior of Reduced Lutetium Diphthalocyanine Film in 0.1M KCl + 0.01M TBACl in Absence and Presence of Oxygen

TABLE 2

OPEN-CIRCUIT DATA FOR DARK BLUE AND VIOLET REDUCTION PRODUCTS IN DEAERATED 0.1M HCl

Color	Reduction Relative to Green	Open-Circuit Time (min)	E (V vs Ag/AgCl) (1M Cl^-)	Predominant Spectral Peak	
				λ_{max} (nm)	A_{max}
Dark Blue	3e	0	-0.152	550	0.500
		0.1	-0.148		--
		10	-0.146		--
		20	-0.145		--
		40	-0.139		--
		60	-0.138		0.479
Violet	4e Probably	0	-0.270	557	0.605
		0.1	-0.261		--
		10	-0.238		--
		20	-0.221		--
		40	-0.201		--
		60	-0.187		0.573

Additional Oxygen Effects. The dark blue and violet reduction products are rapidly oxidized by atmospheric oxygen, sometimes peeling away from the tin oxide in the process. The light blue products formed by 1-electron reduction of the green in HCl or KCl tend to be converted more slowly but cannot be retained for long periods in air.

Figures 6 and 7 include the effects of oxygen on the reduced film containing TBA^+ as the counter ion. This 1-electron product was turquoise blue. Although the open-circuit potential responded promptly to the injection of air, the spectrum scarcely changed in 20 min from that of Curve (b) in Figure 6. Again, it appeared that the large cation led to a slower reaction rate for the film, in this case decreasing its sensitivity to air.

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Manuscript in Preparation:
M. M. Nicholson, "Equilibrium Potentials of the Lutetium Diphthalocyanine Film Redox System in Several Chloride Electrolytes."

VI. PROJECT PERSONNEL

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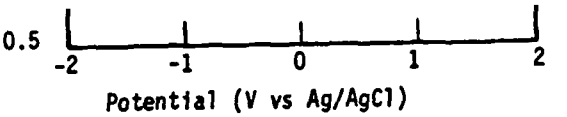

Figure 2. Wide-Span Cyclic Voltammogram for Lutetium Diphthalocyanine/Tin Oxide Electrode in 0.01M HCl